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Process for recovering a polymer in solution

The present invention relates to a process for recovering a polymer in solution.

Polymers are widely used in a variety of forms, primarily in the solid state. Frequently, however, at a given moment in their existence they are in solution in
5 a solvent, from which they must then be extracted. Polymer solutions are encountered, for example, at the end of certain ("solution") polymerization processes, in the course of certain recycling processes, during the cleaning of certain plants for manufacturing polymer-based articles or paints, etc. These polymers in solution are generally recovered by precipitation with a non-solvent.
10 In order to obtain a polymer in a finely divided form and with a particle size which is as fine and regular as possible it is known to perform the said precipitation in the presence of a dispersant.

Thus patent application WO 01/70865 in the name of Solvay describes a process for recycling a plastic by dissolution and precipitation in the presence of
15 a dispersant which is a surfactant such as bentonite, polyvinyl alcohol, cellulose ethers, etc.

The applicant has nevertheless found that some of these dispersants had an adverse effect on the ASG (apparent specific gravity) of the polymer particles obtained and in fact endowed them with a porous character. Moreover, the effect
20 of some of these dispersants may be greatly reduced in the presence of plasticizer. The applicant then found that, surprisingly, by employing at least two dispersants differing in their degree of affinity (i.e. solubility and/or miscibility) with respect to the non-solvent and to the solvent made it possible to lessen these phenomena and to obtain particles exhibiting a high ASG/size ratio.
25 Another surprising advantage of employing a binary dispersant system is that it allows solutions with a relatively high polymer concentration to be treated and also makes it possible to reduce the quantities (rates) of non-solvent that have to be added in order to prevent the particles of precipitated polymer from agglomerating.

30 The present invention accordingly provides a process for recovering at least one polymer in solution in a solvent by precipitation by means of a non-solvent fluid, whereby the precipitation takes place in a precipitation

medium comprising two dispersants of which one (dispersant (I)) has a greater affinity for the non-solvent and the other (dispersant (II)) has a greater affinity for the solvent.

5 The polymer whose recovery is targeted by the process according to the present invention may be of any kind. It may be a thermoplastic resin or an elastomer, but in any case is a resin that can be dissolved in a solvent and which therefore contains little or no crosslinking. It may be an unused (or virgin) resin, which has not undergone any melt-forming except for possible granulation, or a used resin (production waste or recycled resin). It may be an apolar polymer, 10 such as a polyolefin and, in particular, an ethylene polymer (PE) or a propylene polymer (PP). It may also be a polar polymer such as a halogenated polymer and, in particular, a vinyl chloride polymer (PVC), a vinylidene chloride polymer (PVDC) or a vinylidene fluoride polymer (PVDF), etc.; or an EVOH polymer (a copolymer of ethylene and vinyl alcohol). It may also be a mixture 15 of at least two such polymers of the same kind or of different kind. Good results have been obtained with polar polymers, particularly halogenated polar polymers, and very particularly with PVC. By PVC is meant any homopolymer or copolymer containing at least 50 % by weight of vinyl chloride.

20 The polymer dissolved in the solvent may include one or more customary additives such as plasticizer(s), stabilizer(s), filler(s), pigment(s), etc. The term "compound" is generally used for this type of mixture based on polymer(s) and additive(s). One advantage of the process according to the invention is that it allows these additives to be recovered, i.e. to be coprecipitated with the polymer. Thus, for example, where the polymer is PVC, it may be plasticized PVC 25 containing one or more plasticizers generally at a level of 75 % or less, or even 70 % or less, or even 65 % or less. PVC plasticizers are generally organic esters such as phthalates, adipates, trimellitates, etc., with the greatest use being made of phthalates and, in particular, DOP (dioctyl phthalate). The process according to the invention gives good results in the case of plasticized polymers (and 30 plasticized PVC in particular).

The solvent (substance able to dissolve the polymer) is preferably selected from liquids having a solubility parameter (of which a definition and experimental values appear in "Properties of Polymers", D.W. Van Krevelen, 1990 edition, pp. 200-202, and in "Polymer Handbook", J. Brandrup and 35 E.H. Immergut, editors, second edition, p. IV-337 to IV-359 close to that of the polymer to be dissolved and/or having strong interactions with said polymer

(hydrogen bonding for instance). The term "close to" generally means "not differing by more than 6 units". The solvent is generally an organic solvent, preferably a polar solvent such as MEK (methyl ethyl ketone), which gives good results with a large number of polymers and, in particular, with halogenated
5 polymers such as PVC. The non-solvent for its part is preferably selected so as to have a solubility parameter which is different from that of the polymer to be dissolved and having no strong interactions with said polymer. The term "different" generally means "differing by more than 6 units". It will be appreciated that the terms solvent and non-solvent refer not only to simple
10 substances but also to mixtures of substances. Inorganic liquids are highly suitable non-solvents, with water being generally the preferred non-solvent (in the case of polymers which are not water-soluble, obviously) in view of the environmental and economic concerns generally involved in industrial processes. Moreover, water has the advantage of forming an azeotrope with certain polar
15 solvents such as MEK, which makes it easier to remove the solvent by azeotropic distillation.

The solutions that can be treated by the process according to the present invention have a polymer concentration such that their viscosity does not interfere with the proper progress of the process (in particular it is necessary for
20 the non-solvent to be able to be gradually mixed and/or dispersed in the precipitation medium in order for the two to be able to interact and for the precipitation to be able to take place effectively). The presence of dispersants in the precipitation medium makes it possible generally to work with more concentrated polymer solutions (or, more generally, with a higher concentration
25 of compound). Thus it is possible to work with polymer (compound) contents greater than or equal to 100 g per litre of solvent, possibly 200 g/l and sometimes even 300 g/l. However, this content generally does not exceed 500 g/l, or even 400 g/l.

According to the invention a non-solvent fluid is added to the polymer
30 solution, in a quantity sufficient to bring about complete precipitation of the polymer in particle form. It is not detrimental for the non-solvent injected possibly to contain a minority fraction (in weight) of solvent; this is of interest in so far as (as will be set out below for the recycling processes in particular) a possible downstream step of the process may specifically provide such a source
35 of non-solvent, which can therefore be reused without specific purification.

In the process according to the invention, the morphology of the polymer

particles obtained will also be a function of the conditions attached to the addition of the non-solvent : (flow) rate of addition, stirring, pressure, temperature, etc. One way of reducing the size of the polymer particles is to add the non-solvent gradually to the solvent containing the dissolved polymer, with
5 an optimized rate, and to subject the mixture to a shear rate which is likewise optimized as a function of the desired particle size.

Generally speaking, the solvent and the non-solvent are fluids which exhibit miscibility over a certain concentration range only. Indeed, as explained above, it is preferable for the non-solvent to be able to interact with the
10 molecules of solvent and/or of polymer in order to bring about the precipitation and therefore for it to be at least slightly compatible (miscible) with the solvent at low concentration (hence at the start of its addition to the polymer solution). Moreover, solvent and non-solvent are often liquids having a very different chemical structure (so as to be compatible and incompatible, respectively, with
15 the polymer) and, consequently, their miscibility is rarely total. Also, in general, in the course of gradual introduction of non-solvent to the polymer solution, there occurs first of all a phase separation - that is, at a given moment, there is transition from a single-phase medium consisting of a solvent-rich phase containing the dissolved polymer and a small amount of non-solvent to a two-
20 phase medium consisting on the one hand of a solvent-rich continuous phase in which the polymer is dissolved and on the other hand of a disperse phase consisting of droplets rich in non-solvent. Subsequently, following the addition of a given quantity of non-solvent (determined by the phase diagram between solvent and non-solvent), there is generally a phase inversion - that is, the
25 continuous (majority) phase then becomes the phase rich in non-solvent, and the disperse phase then consists of droplets of solvent-rich phase containing the dissolved polymer.

With certain polymers such as halogenated polymers and PVC in particular (and more particularly using, respectively, MEK and water as solvent and
30 non-solvent) the applicant has found that, although the precipitation of the polymer begins with this phase inversion, the morphology of the polymer particles obtained is in fact essentially independent of the steps prior to this inversion and is in contrast primarily dependent on the operating conditions during and after the phase inversion.

35 An important event in the process according to the invention is therefore the phase inversion. According to one preferred version of the present invention

the composition at phase inversion is approached by addition of non-solvent in liquid form. This is because the injection of vapour only in fact has a positive effect on the morphology of the polymer particles during or after the phase inversion, and it is therefore not useful for the non-solvent to be in vapour form before that stage. According to this version the non-solvent is initially introduced into the precipitation medium in liquid form only and in a quantity (Q') which is not zero but is less than the quantity (Q) required to bring about the phase inversion, and is subsequently introduced into the precipitation medium at least partly in vapour form. The quantity (Q), which depends on the nature of the solvent and non-solvent, on the temperature, on the pressure and, in certain cases, on the quantity of dissolved polymer is easily determined experimentally. All that need be done is to gradually introduce the non-solvent in liquid form into the solution until phase inversion is observed (which is readily identifiable for the person skilled in the art) and to measure the quantity of non-solvent added at this point, which is the quantity Q . Good results have been obtained with a quantity Q' of greater than or equal to 50 % (by volume) of the quantity Q , or greater than or equal to 70 %, or even to 90 %. It should be noted that the term "precipitation medium" refers to the medium in which the polymer precipitates and which to start with contains solely the polymer and the solvent and, subsequently, as they are introduced, the dispersants, the non-solvent, the additives, etc.

According to the invention precipitation must take place in the presence of two different dispersants and, preferably, the time of introduction of these dispersants is optimized as a function of the progress of the precipitation. A dispersant is a substance which promotes the dispersion of a discrete phase (which may be formed either of liquid droplets or of solid particles) in another phase, the continuous phase. The said substance generally acts at the interface between the two phases and it prevents the agglomeration of the discrete phase (in other words, it promotes the production of a fine and regular dispersion).

Thus in one advantageous version of the process according to the invention the dispersant having the higher affinity for the non-solvent (I) is primarily added to the precipitation medium before the phase inversion, so as to be present during the said inversion. By "primarily" is meant in a majority weight fraction (relative to the total quantity of the dispersant (I) added during the process), i.e. greater than 50 %, but which may be greater than or equal to 70 % or even 90 % by weight. With particular preference the entirety of the dispersant (I) will be

added to the precipitation medium before the phase inversion.

Similarly, according to another advantageous version of the process according to the invention, the dispersant having the higher affinity for the solvent is primarily added to the precipitation medium after the phase inversion, the term "primarily" being defined as before. This because the applicant has found that the fact that it is present in excessive quantities before and during the phase inversion increased the porosity (and hence impaired the ASG) of the polymer particles.

Optimizing the nature and the time of introduction of the dispersants makes it possible to optimize the morphology of the particles and hence to obtain a compact powder of small particles.

Good results have been obtained by adding the entirety of the dispersant (I) and a minority weight fraction (for example greater than or equal to 10 % or even 15 % or better still 20 %, but less than 50 % or even 40 % or better still 30 %) of the dispersant (II) after the polymer has dissolved and before the non-solvent is added, and the remainder of the dispersant (II) after phase inversion.

The dispersant (I) described above is generally used in a quantity which is at least equal to that of the dispersant (II) or even greater than the quantity of the dispersant (II) by a factor greater than or equal to 2 or even 3. The amount of dispersant (I) is generally greater than or equal to 0.01 % by weight relative to the weight of polymer, preferably greater than or equal to 0.05 % or better still greater than or equal to 0.1 %. The amount of dispersant (I) is generally less than or equal to 5 % or even 2 % or better still 1 %.

The dispersants used in the process according to the invention may be of any kind whatsoever. However, especially when the non-solvent is water, the dispersants are advantageously selected from cellulose ethers and polyvinyl alcohols. In the frame of the present invention, "water" in fact designates an aqueous medium having a majority weight fraction of water (hence, containing more than 50 %, even more than 60 % and preferably, more than 70 % in weight of water). It is preferably pure water or water containing a minority weight fraction of solvent. Among cellulose ethers, substituted methylcelluloses and, in particular, those substituted by hydroxypropyl groups give good results. However, better results are generally obtained with polyvinyl alcohols (POVAL). In this case the dispersants (I) and (II) have degrees of hydrolysis (DH, measured by hydrolysing the acetate groups with a base (NaOH) and by

titrating the unreacted base with an acid (HCl) which are different, the dispersant (I) having a DH greater than that of the dispersant (II). Good results have been obtained when the dispersant (I) has a DH greater than or equal to 65 %, or 67 % or even 70 %, but less than or equal to 90 % or even 85 % or better still 80 %. Good results have likewise been obtained when the dispersant (II) has a DH less than or equal to 60 % or even 55 %. Particularly advantageous results are obtained when the dispersants (I) and (II) both have DHs contained within the aforementioned ranges.

Another important parameter when selecting dispersants in general and POVAL in particular is their viscosity in aqueous solution. Accordingly the viscosity of a 4 % solution of dispersant at 20°C (expressed in mPa.s) is :

- for dispersant (I), advantageously from 1 to 300, or even from 1.5 to 250, or better still from 2 to 200;
- for dispersant (II), advantageously from 1 to 20 000, or even from 1.5 to 10 000, or better still from 2 to 5000.

Generally, when precipitation is at an end, the product present comprises a suspension of polymer particles in a medium which is rich in non-solvent. The weight proportion of solid particles in this suspension may be greater than or equal to 10 % or even 20 % or even 30 % without any agglomeration of the said particles, the presence of dispersants being beneficial from this viewpoint. However, this proportion does not exceed advantageously 80 % or even 65 % or better still 50 %.

The polymer particles present in the suspension are collected by any appropriate means : thermal (evaporation of the solvent, optionally by azeotropic distillation : see above), mechanical (filtration, centrifugation, etc.) or a hybrid form (atomization, for example). In the case of temperature-sensitive polymers (such as PVDC, for example) preference will be given to mechanical methods. The particles collected may then be washed, dried and treated by any known means prior to storage, sale and/or use.

The polymer solution to which the present invention is applied may be obtained by any suitable means. However, the dissolving of the polymer in the solvent takes place generally under a pressure at least equal to atmospheric pressure or even at least equal to 1.5 bars. Advantageously this pressure does not exceed 10 bars, preferably 5 bars.

The dissolving temperature is generally at least 75°C or even 100°C; generally it does not exceed 125°C or even 110°C.

In the course of this dissolving it may prove to be advantageous to work in an inert atmosphere, under nitrogen for example, in order to avoid any risk of explosion or of degradation of the solvent and/or of the non-solvent.

During or after the dissolving of the polymer, but before precipitation, it is possible to add one or more additives to the solution. An additive for the purposes of this version of the invention is any organic or inorganic compound not present in the original plastics, or present in a quantity lower than that which is desired. Possible inorganic additives include inorganic pigments, carbon black, metal powders, nanoparticles of various kinds, etc. Possible organic additives include organic pigments, stabilizers, oligomers, plasticizers, etc.

The process according to the present invention can be integrated into any process involving the recovery of a polymer from a solution. In particular it may form part of a process for recycling articles based on polymer(s). The present invention accordingly likewise provides a process for recycling at least one article based on at least one polymer, whereby

- a) if necessary, the article is shredded into fragments with an average size of 1 cm to 50 cm
- b) the article or the fragments of article is or are contacted with a solvent capable of dissolving the polymer
- c) the polymer in solution is recovered using the process described above.

The articles in question may be single-layer or multi-layer solids of any form (sheet, plate, tube, etc.); they may include a number of polymers (only one of which, generally, will then be dissolved selectively, although the article may likewise serve for the manufacture of an alloy) and also non-polymeric materials (reinforcements, fixings, etc.) which will then be removed before the solution is treated by the process described above.

It should be noted that, in the case of articles based on a number of polymers, it may prove advantageous to remove the other (or one of the other) polymer(s) before dissolving the polymer it is desired to recover. Thus, for example, if the solvent selected is able to dissolve a number of the polymers in the article, it may prove advantageous first to eliminate the interfering polymer, for example by means of another solvent, which does not dissolve the polymer to be recovered. It should be noted that, when one of the polymers is semi-crystalline, its solubility may be lowered by an afterbake (that is, residence at a temperature and for a time suitable for obtaining maximum crystallization). An example of such polymers is given by PVC (an amorphous polymer) and PVDC

(a semi-crystalline polymer). Thus, for example, an afterbake treatment (lasting for 1 h at 70°C or for 2 days at 40°C, for example) on a PVC/PVDC complex makes it possible to render the complex insoluble in MEK at 50°C and hence to dissolve the PVC selectively in MEK at 50°C (or even at 75°C) and to apply the process as described above to the resulting solution. It should also be noted that the composition of the solvent may be adapted in order to dissolve certain polymers of a structure selectively.

In the recycling process described above the conditions (pressure, temperature, stirring, etc.) in which the polymer is dissolved and in which, optionally, non-polymeric elements or elements based on an interfering polymer are separated before precipitation (by filtration, prior dissolution, etc.) will be optimized by any means known to the person skilled in the art. Teaching useful for this purpose is given in Applications EP 945481, WO 01/23463 and WO 01/70865 in the name of Solvay, and is incorporated by reference into the present application.

A major advantage of such a recycling process is that it is able to function in a closed loop (either continuously or batchwise, but with quasi-total recirculation of the liquid phase, with the exception of losses due in particular to adsorption on the polymer particles obtained), without generating refuse. Indeed, the liquid medium obtained after precipitation and separation of the polymer particles, which consists primarily of non-solvent (generally containing the dispersants), may be recycled, where appropriate by means of appropriate treatment. This treatment may consist in one or more distillations, flocculations (in order to remove and/or recover the dispersants), decantations, washings, etc., and in combinations of these treatments. Similarly, when the solvent has been removed from the precipitation medium by azeotropic distillation with the non-solvent, the vapours resulting from this distillation may be condensed and may constitute a liquid phase which can be treated as described above. This treatment preferably includes at least one decantation and, in that case, it is advantageous for the said decantation to proceed at least partly in the presence of a phase separation agent. Thus where two or more decantations take place (in parallel or in series) it is advantageous for at least one of them to take place in the presence of a dispersant.

A recycling process of this kind has been successfully applied to articles containing PVC.

**Reference Examples R1, R2 and R3 (not in accordance with the invention)
and Examples 4 to 9 (in accordance with the invention)**

5 A solution containing 11 % by weight of PVC plasticized with DOP (PVC of Kw 71 with 25 % by weight of DOP) in MEK was prepared (in 1 hour at 75°C under atmospheric pressure and with a helical stirrer rotating at 250 revolutions/min).

A number of fractions of this solution were withdrawn, and were subjected to precipitation under the following conditions :

- 3500 g of solution were heated to 75°C
- 10 – stirring was then started and was increased to a speed of 1000 revolutions/minute, and 2.6 kg of vapour were introduced for 40 minutes in order to evaporate the solvent and to cause the PVC compound to precipitate
- the solvent was recovered by condensation for re-use
- 15 – the PVC compound in suspension in water was filtered on a 125 µm metal filter and then dried in an oven under vacuum (0.2 bara) at 80°C for 5 hours
- the powder of precipitated PVC compound was subsequently screened on a 1 mm sieve.

20 The dispersants tested are Poval® L9 (dispersant I; polyvinyl alcohol of DH = 71 %) and Poval® LM10HD (dispersant II; polyvinyl alcohol of DH = 40 %). These dispersants were used in various ways (in terms of concentration and time of introduction), which are detailed in the table below.

25 The result of these tests likewise features in this table, which reproduces the final concentration of PVC in the suspension (in weight % relative to the total weight of the suspension), the type, quantity and mode of introduction of the dispersants, the ASG (in g/cm³) and the average diameter (in µm) of the particles obtained, and also the ratio of these 2 parameters, which constitutes an index of the quality of the polymer particles obtained.

Example	[PVC] _{suspension} (weight %)	Poval® L9 direct (weight %)	Poval® LM10HD direct (weight %)	Poval® LM10HD differentiated (weight %)	ASG (g/cm ³)	Average diameter (d) (µm)	ASG/d
R1	11	0.3	-	-	580	390	1.48
R2	11	-	0.3	-	450	310	1.45
R3	18	0.3	-	-	620	510	1.22
4	11	0.3	0.1	-	460	275	1.67
5	11	0.3	0.3	-	410	250	1.64
6	11	0.3	-	0.3	520	285	1.82
7	11	0.3	0.05	0.25	505	260	1.94
8	11	0.3	0.02	0.28	480	270	1.78
9	18	0.3	0.05	-	630	320	1.97

Direct = introduction during dissolution

Differentiated = introduction after phase inversion